COMPARISON OF COMPOUNDING APPROACHES FOR WOOD-DERIVED CELLULOSE NANOCRYSTALS AND POLYAMIDE 6

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Abstract

A simple, water-assisted approach to compounding cellulose-nanocrystal-reinforced polyamide 6 was investigated and compared to solvent blending using formic acid and melt compounding using freeze-dried CNCs. The watter-assisted approach did not result in any apparent degradation of the CNCs during compounding and dispersion improved in the following order: freeze-dried compounding < water-assisted compounding < solvent blending. Improved dispersion resulted in less thermal degradation during injection molding and improved tensile properties. Future work to improve both the processing and performance of these composites is suggested.

Introduction

Reinforcing thermoplastics with carbon or glass fibers is often used as a means to improve the performance of thermoplastics, allowing them to be used more efficiently and expand into a broader range of applications. However, there has been recent interest in sourcing reinforcing fibers from renewable, natural resources. For example, composite manufacturers are seeking to take advantage of the favorable balance of properties (e.g., low density, good mechanical properties) of bast fibers from plants in composite applications in automotive, packaging, sporting goods, and furniture applications [1-5]. Because of the limited thermal stability of biobased fibers, using them as reinforcements in engineering plastics such as polyamide 6 (PA6) is challenging. To improve the thermal stability, the less thermally stable components of biobased fibers (e.g., lignin, hemicellulose, extractives) can be removed and, through careful processing, PA6 composites can be prepared without the need for plasticizing the polymer and potentially altering its properties. For example, Sears, et al. [6] were able to reinforce PA6 with various high-purity cellulose fibers that increased flexural strength by about 50-75%. Kiziltas, et al. [7] also found that adding 30% of a highly crystalline, commercial microcrystalline cellulose increased the dynamic storage modulus by about 25%.

Nanocellulose-based reinforcements constitute a new class of these biobased reinforcements. Trees, plants, some marine creatures such as tunicates, and certain bacteria and algae form microfibrils from cellulose molecules [8]. These microfibrils have a complex structural hierarchy and often act as the main reinforcing element in their respective organisms. In part, it is the high reinforcing potential of native crystalline cellulose within these microfibrils that has recently led researchers to extract nanocellulose from them for use in composites. A variety of nanocelluloses can be prepared, most often through a combination of mechanical and chemical or enzymatic treatments. Key attributes such as strength, aspect ratio, crystallinity, and surface functionality are strongly influenced by preparation method. Nanocellulose and their composites have been recently reviewed [8, 9].

Here we focus on wood-derived *cellulose nanocrystals* (CNCs) also called *cellulose whiskers*, *nanowhiskers*, or *nanorods*. They are produced through transverse cleavage of cellulose by acid hydrolysis. This results in high modulus, rod-like structures with aspect ratios of around 10-100 depending on the source of the cellulose and the exact preparation conditions [7]. Plant-based sources yield crystallites with diameters of about 5 nm and lengths typically about 100-400 nm and lengths as high as several micrometers [29]. A transmission electron micrograph of CNCs is shown in Figure 1.

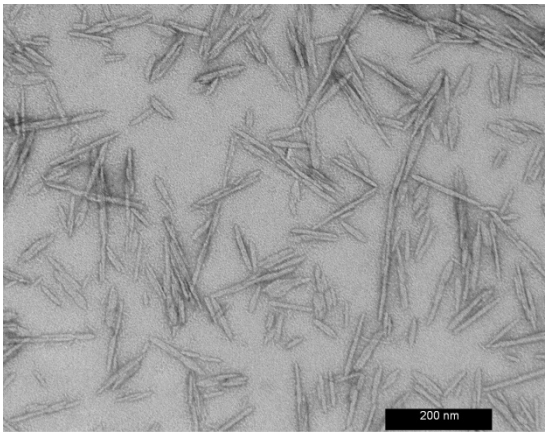

Figure 1: TEM of CNCs from wood.

Unfortunately, preparation of nanocellulose typically involves chemical treatments that result in modification of the cellulose, which often reduces thermal stability. For example, CNCs are most often prepared through sulfuric acid hydrolysis, which results in sulfation of the hydroxyl groups reducing thermal degradation temperature [10]. This reduction in thermal stability can be offset somewhat by attachment of a counter ion such as sodium [11]. However, this improvement is still insufficient to allow conventional melt compounding with PA6. Also, the preparation of nanocellulose typically results in an

aqueous dispersions and the water needs to be removed before or during compounding without agglomeration of the nanocellulose, which readily hydrogen bonds during drying.

Because of the thermal stability and dispersion challenges, several researchers have opted for a solvent blending approach to incorporate CNC into PA6 in composite films [12]. Qua et al. [12] combined an aqueous CNC solution with a 90% formic acid solution in which PA6 had previously been dissolved. After stirring for 30 minutes, the solution was cast into petri dishes and dried. The resulting films contained 5% CNC and showed an increase in tensile modulus of about 20% over neat PA6 films and an increase in tensile strength of about 90-120%, depending on the cellulose source (either flax or microcrystalline cellulose). However, the mechanical properties appear quite low for PA6 (e.g., tensile strength of 20-50 MPa), possibly because film casting was used to prepare the specimens rather than a melt processing approach (e.g., injection molding). To increase thermal stability so that they could be melt processed with PA6, Corrêa et al. [13] first coated CNCs with PA6 by dispersing freeze-dried CNCs into formic acid and then dissolving PA6 into the dispersion, followed by drying. A 2:1 PA6:CNC weight ratio was used. The PA6-coated CNCs were then compounded with additional PA6 in a twin screw extruder and injection molded. The final composites, which contained 1% CNC, had a 30% higher tensile modulus than neat PA6 processed in the same manner. However, strength was not improved and elongation at break was reduced by 55%. In summary, an efficient, melt processing method that uses a more benign solvent (e.g., concentrated formic acid is highly caustic) or no solvent but yet realizes the reinforcing potential of nanocellulose has thus far remained elusive.

However, since PA6's melting temperature can be lowered by about 60°C by addition of water, CNC-PA6 composites are a good candidate for water-assisted compounding, especially considering that the CNCs are already in an aqueous dispersion. Similar approaches have been used to prepare PA6-nanoclay composites, for example [14, 15].

In this study, a simple, water-assisted compounding approach was investigated in which a thermokinetic mixer was used to prepare CNC reinforced PA6 composites. This compounding approach was compared to 1) solvent blending using formic acid and 2) melt compounding using freeze-dried CNCs.

Materials

Formic acid and a low molecular weight PA6 (Nylon 6) were obtained from Sigma Aldrich (Milwaukee, WI). The PA6 had a melting point of 228.5°C and a density of 1.08g/cm^3. The CNCs were produced in the Forest Products Laboratory's nanocellulose pilot plant. Briefly, commercially available dissolving pulp dry lap made from southern pine was used as the starting material for producing the CNCs. Strips of the dissolving pulp were reacted with 64% sulfuric acid at 45°C for approximately 1.5 h under a nitrogen blanket with constant stirring. The hydrolysis reaction was terminated by diluting with water to approximately a 10-fold volume of the initial suspension. The CNC were neutralized by adding an aqueous sodium hydroxide solution of about 5% concentration. At this point, the CNC were not colloidal and settled due to the high salt concentration. Continued dilution and decanting were carried out until the sodium sulfate concentration was about 1%. The sodium sulfate and other salts were removed by ultrafiltration in a tubular ultrafiltration unit. Fresh water was added to the suspension during ultrafiltration to keep the CNC concentration at approximately 1%. After essentially all of the salt was removed, the CNC suspension was concentrated in the same ultrafiltration unit. The final concentration of the CNC was 2.5% by weight [16]. For the solvent blending and dry compounding approaches, the CNCs were freeze-dried by placing chilled suspensions into a tray freeze dryer (VirTis model 36DX84, SP Scientific, Warminster, PA) set to -20°C. The process was stopped once the material was dry, as indicated by the rapid changes in the operating pressure and temperature of the chamber.

Three methods of compounding were investigated to incorporate the CNCs into PA6. In the solvent blending approach, 2.1 grams of FD-CNC were added to 400 ml formic acid (Sigma Aldrich 88%) and sonicated for 30 min at approximately 100W. Sufficient PA6 was added to yield a PA6:CNC weight ratio of 95:5. The mixture was stirred for 1 hour and then slowly poured into water to precipitate it. The precipitate was then filtered and washed until neutral. The precipitate was then air-dried and milled (Laboratory Wiley Mill, ArthurH. Thomas Co., Philadelphia, PA) using a 10 mesh screen followed by oven-drying at 105°C. Also, PA6 was dissolved into formic acid without CNCs and was precipitated, filtered, washed and dried. This was used as a matrix material in the other two compounding methods to remove any effects of the formic acid on matrix properties so that the compounding methods could be more directly compared.

In the water-assisted approach, 38 grams of PA6 and 80g of the 2.5% aqueous CNC solution were added to a 1 liter, thermokinetic mixer (K Mixer, Synergistics, Inc., St. Remi de Napierville, Quebec). The blend was then compounded at 5500 RPMs (tip speed of about 37 m/s) and a discharge temperature of 185°C as measured by an infrared sensor mounted flush with the inside of the mixing chamber. Batch times were approximately 2 ½

minutes. The compound was then cooled, milled, and oven dried at 105°C.

In the third approach, freeze-dried CNCs were dry compounded with PA6 in the thermokinetic mixer at 5500 RPMs and a discharge temperature of 230°C, after which it was cooled, dried, and milled as in the water-assisted approach.

The thermal stability of the milled compounds was investigated by thermogravimetric analysis (TGA7; Perkin Elmer Corporation, Boston, MA). Approximately 6-8 mg of compound was dried at 105°C for at least 4 h prior to testing. Temperature scans from 50 to 650°C were performed with a heating rate of 10°C/min.

All three of the compounds were molded using a microcompounder and microinjection molder (DSM Xplore system, DSM Research, Geleen, Netherlands) Compounder barrel temperatures were set at 220°C, 230, and 240°C and the screw speed was 50 RPMs. A nitrogen blanket was used to minimize degradation. The material was transferred to the injection molder and Type V tensile specimens [17] were molded at 230°C at 10 bars of pressure for 10 seconds.

For coarse evaluation of CNC dispersion, 30μm thick sections microtomed from the necked portion of the tensile specimens transverse to the flow direction were analyzed under polarized light (Orthoplan-POL polarizing microscope, Leitz Wetzlar, Germany). Tensile properties were measured according to ASTM D638-10 [17] on a test machine (Instron 5556, Norwood, MA, USA) equipped with a 500 N load cell in conjunction with an MTS LX 500 noncontact laser extensometer (MTS Systems Corporation, Eden Prairie, MN) to measure strain.

Discussion

A thermokinetic mixer is a high-intensity batch mixer comprised of a mixing chamber and high speed rotors that impinge materials against the interior of the mixing chamber, which induces rapid heating and mixing of the materials being compounded. A thermokinetic mixer was chosen as the compounder for the initial exploration of water-assisted compounding because of its high mixing intensity (both before and after melting), rapid temperature increase, and small batch size.

The water content before thermokinetic mixing was 66%, well above the threshold of about the 30% necessary for maximum melting temperature reduction found by Wevers et al. [18] in sealed capsules. While the thermokinetic mixer is not completely sealed and much (though not all) of the water was flashed off as steam during the batch cycle, we found that the high initial water content, high rotor speed, and rapid temperature rise was sufficient to melt the PA6 and compound the CNCs into it before the discharge temperature of 185°C was reached. Batch times were typically about 2 ½ minutes and no obvious discoloration of the material was seen (Figure 2). There was some discoloration of the material that was prepared by simply dry compounding freeze-dried CNCs into PA6 due the higher temperatures required, despite the short batch time.

Figure 2: Compounded material produced by the water-assisted compounding approach after milling.

The thermal stability of starting materials as well as the compounds prepared by all three approaches were analyzed by thermogravimetric analysis (TGA). Figure 3 shows typical weight loss curves for CNCs with sodium counter ions. The ash content at 650°C was about 32% of the original weight of the CNCs. This would correspond to about a 1.6% ash content in the composites, which was what was found suggesting that the CNCs were not lost during the various compound approaches. The weight losses for the CNCs begin at considerably lower temperatures than in the compounds. However, how much of this shift is due to encapsulation slowing the release of volatiles versus an actual slowing of the degradation processes is not clear. The comparison of the onset of weight loss of the compounds is perhaps the most useful measure of thermal stability. This section of the graphs (encircled region) is enlarged in Figure 4.

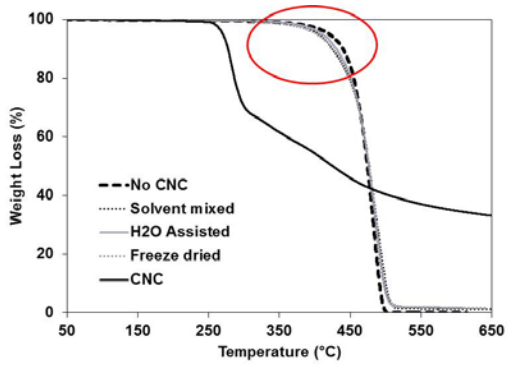

Figure 3: Thermogravimetric analysis of the original CNC, unfilled PA6 ("no CNC"), and PA6-CNC composites compounded by the three approaches. A close up view of the encircled region is shown in Figure 4.

The small and slightly variable weight losses below 300°C are probably due to moisture losses since some moisture sorption when transferring the materials from the vacuum oven and beginning the TGA scans is likely. Above 300°C, the compounds prepared by solvent mixing and water-assisted approaches appear to behave similarly. However, the compound prepared by the freeze-dried approach appears to degrade at lower temperatures, possibly due to poor dispersion/encapsulation.

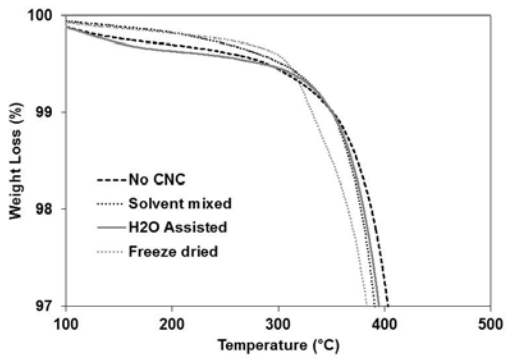

Figure 4: Close up of the encircled region of the TGA curves in Figure 3.

Despite the nitrogen blanketing, the relatively low extrusion and molding temperatures, and the short processing times, CNC did degrade somewhat during injection molding as shown by the darkening of the specimens shown in Figure 5, with the specimen prepared by freeze-drying showing the most degradation. This was not entirely unexpected given the high processing temperatures and alternative approaches to specimen fabrication under investigation.

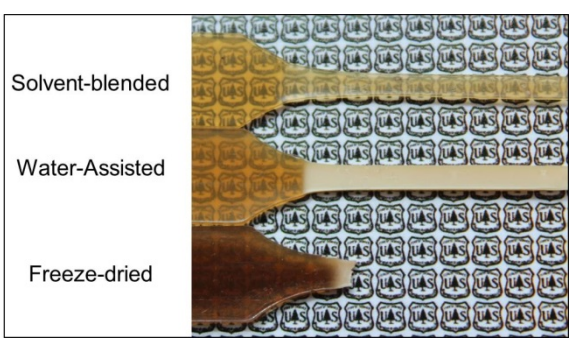

Figure 5: Injection molded specimens after tensile testing.

As a coarse assessment of dispersion, transverse sections were cut from the necked portion of the tensile specimens and were examine by polarized light microscopy. The specimens prepared by the dry compounding of freeze-dried CNCs into PA6 showed the worst dispersion by far (Figure 6). Although the dispersion prepared by water-assisted compounding was much improved, it was not as good as the solvent-blended specimen.

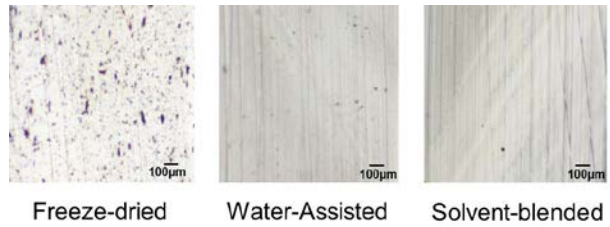

Figure 6: Polarized light micrographs of sections from PA6-CNC composites.

The appearance of the tensile fractured specimens supports the polarized light microscopy findings (Figure 5). The specimens prepared by the freeze-dried compounding method fractured at low strains presumably due to stress concentrating at the large agglomerates. The specimens prepared by solvent blending had large strains and maintained transparency as the specimen necked while those prepared by water-assisted compounding demonstrated stress whitening likely due to cavitation created by small agglomerates.

Similar trends were found for both tensile modulus and strength, although the magnitude of the effects was different. Addition of freeze-dried CNCs to PA6 did little to affect its tensile properties (Figure 7) except for a reduction in strain at break (Figure 5). Improvements in modulus of 17% and 45% were found for water-assisted and solvent mixed composites, respectively, but were only 7% and 13% for strength. The lack of reinforcement even in well dispersed CNC composites is possibly due to limited aspect ratio (Figure 1) and limited adhesion between the PA6 and CNCs. Differential scanning calorimetry on transverse sections microtomed fom the tensile specimens showed little difference between unfilled PA6 and the composites in the 1st heating scans (not shown). This suggests that the CNCs had little effect on crystallization so the changes in tensile properties are unlikely to be due to nucleation effects, for example. Consequently, surface treatments are currently being explored to improve both the reinforcing ability of the CNCs and their dispersability. Also, modifications to the CNC preparation procedure to maintain aspect ratio are also being studied.

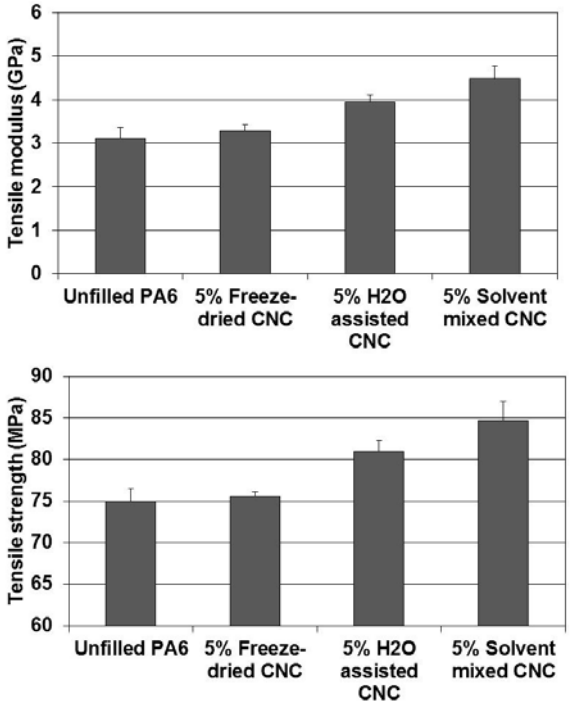

Figure 7: Summary of tensile properties of PA6-CNC composites.

Conclusions

A simple, water-assisted approach to compounding CNC reinforced PA6 composites was possible using a thermokinetic mixer with little apparent degradation of the CNCs. The resulting dispersion was an improvement over a simple dry compounding approach with freeze-dried CNCs but was not as good as in a solvent blending approach. Little effect on crystallinity was found with addition of CNC. Regardless of the compounding approach, increased aspect ratio and improved adhesion between CNC and PA6 is necessary to improve reinforcement. Also, modified or alternative specimen molding approaches (e.g., microcellular injection molding) need be investigated in order to avoid thermal degradation.

Acknowledgements

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